

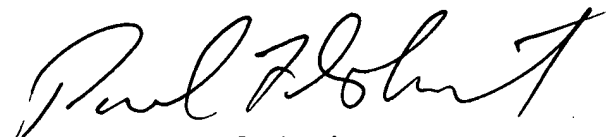
Remarks

Claims 30-55 are added and claims 1-29 are cancelled herein.
Claims 30-55 will be pending upon entry of this amendment.
Favorable consideration and allowance of claims 30-55 are respectfully requested.

A check in payment of the applicable excess claims
fee is enclosed.

A marked-up version and a clean copy of the substitute
specification are enclosed. The substitute specification
contains no new subject matter.

Respectfully submitted,



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MARKED-UP VERSION
METHOD FOR ELECTRODEPOSITION OF BRONZES

——FIELD OF THE INVENTION

[0001] This invention concerns a method for electrodeposition of bronzes, with which the substrate to be coated is plated in an acid electrolyte that contains at least tin and copper ions, an alkylsulfonic acid and a wetting agent, and the preparation of such an electrolyte.

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BACKGROUND OF THE INVENTION

[0002] Methods for deposition of tin and tin alloys on the basis of various types of electrolytes are known from the prior art and are already widely used in practice. Methods for deposition of tin and/or tin alloys from cyanide electrolytes are very common. Such electrolytes, however, are highly toxic, which makes their use problematic from the environmental standpoint, so that for some years there has been a push to develop cyanide-free electrolytes, for example electrolytes based on pyrophosphates or oxalates, which operate in a pH region of 5--9. However, such methods have both economic and technical disadvantages, of which the relatively slow deposition rates may be mentioned here.

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[0003] For these reasons development is currently going mostly in the direction of making available methods for deposition of tin and/or tin alloys from acid electrolytes, since, for one thing, divalent tin can be very easily reduced to metallic tin in acid electrolytes, which leads to better deposition rates while having qualitatively equivalent coatings, and for another the disadvantageous effect of alkaline electrolytes on substrates, for example ceramic structural elements, is prevented by this.

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[0004] Thus, acid electrolytes and methods for deposition of qualitatively high grade tin or tin alloys with a higher deposition rate are known from EP 1 111 097 A2 and US 6,176,996 B1. These are electrolytes that contain at least two divalent metal salts of an organic sulfonic acid and from which are deposited solderable and corrosion resistant coatings that can be used, for example, as substitutes for lead-containing solderable coatings in electronics for manufacture of circuit boards, etc.

[0005] However, such methods have their limits in the deposition of tin-copper alloys with high copper contents, such as the so-called "true" bronzes, which have a copper content of at least 10%. For example, due to the high difference of potential between tin and copper higher rates of oxidation of the divalent tin can occur, due to which it very easily becomes oxidized to tetravalent tin in acid electrolytes. However, in this form tin can no longer be electrolytically deposited in an acid and thus is withdrawn from the process, which leads to uneven deposition of the two metals and to a decrease of the deposition rate. In addition, oxidation to tetravalent tin leads to increased sludge formation, which can prevent stable operation and long lifetime of the acid electrolyte. Moreover, because of such contaminated of a firmly bonding and pore-free coating is no longer guaranteed.

[0006] Because of such technical process disadvantages, there is currently no large area of use for electrolytically deposited bronze coatings. Occasionally bronze coatings are used in the jewelry industry as a substitute for expensive silver or allergy-triggering nickel. In the same way methods for electrodeposition of bronzes are also gaining importance in some technical fields, for example in electronics for coating electronic components or in mechanical engineering

and/or in process technology for coating bearing overlays and friction layers. However, in this case chiefly white bronzes or the so-called "false bronzes," whose copper content can be kept quite low due to process conditions, are deposited as nickel substitutes.

[0007] Therefore, the invention is based on the task of providing a method for deposition of bronzes that, in contrast to the methods known from the prior art, enables uniform deposition of at least tin and copper side by side from an acid electrolyte at considerably higher deposition rates. Moreover, with this method firmly bonding and pore-free bronze coatings with high copper contents as well as various decorative and mechanical properties are said to be deposited.

SUMMARY OF THE INVENTION

[0008] In addition, an acid electrolyte that can have a high content of divalent copper ions, is stable with respect to oxidation-caused sludge formation, and is both economical and environmentally friendly when used over a long period of time, is to be made available.

[0009] The task is solved in accordance with the invention by a method of the kind mentioned at the start, which is characterized by the fact that an aromatic, nonionic wetting agent is added to the electrolyte.

[0010] With this invention a method for electrodeposition of bronzes is made available, where an anode of a copper-tin alloy and a cathode are connected to the substrate that is to be coated by means of an electrolyte, and coating takes place by passing a direct current through them. In addition, with the invention an electrolyte that is usable in particular for this method and the coatings that are obtainable by this method are made available.

[0011] Through the method in accordance with the invention the disadvantages known in the prior art are remedied with the offering of a new electrolyte composition and in this way considerably better deposition results are achieved. Moreover, the conduct of the method is made to be simpler and more economical. This, too, is chiefly based on the advantageous composition of the electrolyte. For example, the method is carried out at room temperature, or between 17 and 25°C, and the substrate to be coated is plated in a highly acid environment at a pH <1. The electrolyte is particularly stable in this temperature range. In addition, there are no longer any costs for heating the electrolyte and the plated substrates also do not have to be cooled very much, with large expenditures of time and money. Moreover, deposition rates of 0.25 ~~mm/min~~ mm/min at a current density of 1 A/dm² are achieved due to, among other things, the pH value and the advantageous addition of at least one aromatic non-ionic wetting agent. By increasing the metal content this rate can be raised up to 7 A/dm² in rack operation and even up to 120 A/dm² for continuous plants. Thus, usable current densities in a range from 0.1--120 A/dm² are reached in each case according to plant type.

[0012] Surprisingly, the wetting of the surfaces to be plated, above all those of more complex substrates, is considerably improved in particular through the addition of at least one aromatic nonionic wetting agent to the electrolyte. This advantageously has the result that not only are the considerably higher deposition rates achieved through the use of the method in accordance with the invention, but moreover the coatings produced by the method are uniform and qualitatively high grade, have very good adhesion and are generally pore-free.

[0013] Another advantage of the aromatic nonionic wetting agent that is used is that because of the advantageous wetting properties the electrolyte and/or the substrate in the electrolyte need to be agitated only a little or even not at all, in order to achieve the desired deposition results, so that additional devices for agitation of the electrolyte can be omitted. In addition, because of the advantageous use of the aromatic nonionic wetting agent, electrolyte residues drain from the plated substrate better when it is removed from the electrolyte, which leads to reduced entrainment losses and thus to lower process costs.

[0014] The addition of 2--40 g/L of one or more aromatic nonionic wetting agents is especially advantageous, with ~~naphthol~~ naphthol-~~ethoxylate~~ naphthol ethoxylate and/or nonylphenol ethoxylate are especially preferably used.

[0015] The proposed method is therefore advantageously economical and environmentally friendly compared to the cyanide processes.

[0016] The additional use of one or more anionic and/or aliphatic nonionic wetting agent that is known from the prior art is also optionally possible, provided these wetting agents support or even enhance the advantageous effects of the aromatic nonionic wetting agent. In this regard polyethylene glycols and/or anionic surfactants are preferably added to the electrolyte as anionic and/or aliphatic nonionic wetting agents.

[0017] As already mentioned above, the method in accordance with the invention is characterized in particular by the special composition of the electrolyte. It contains essentially tin and copper ions, an alkylsulfonic acid and an aromatic nonionic wetting agent. In addition, stabilizers

and/or complexing agents, anionic and/or nonionic, aliphatic wetting agents, oxidation inhibitors, brighteners, and other metal salts can optionally be contained in the electrolyte.

[0018] The metals that are primarily added to the electrolyte for deposition of bronzes in accordance with the invention -- tin and copper -- can first and foremost be in the form of salts of alkylsulfonic acids, preferably as methanesulfonates, or as salts of mineral acids, preferably as sulfates. Tin methanesulfonate is especially preferably used as tin salt in the electrolyte preferably in an amount of 5 -195 g/L of electrolyte, preferably 11--175 g/L of electrolyte. This corresponds to a use of 2--75 g/L, preferably 4--57 g/L divalent tin ions. Copper methanesulfonate is especially preferably used in the electrolyte as the copper salt, which is advantageously added to the electrolyte in an amount of 8--280 g/L of electrolyte, preferably 16--260 g/L of electrolyte. This corresponds to the use of 2--70 g/L, preferably 4--65 g/L divalent copper ions.

[0019] Since the deposition is clearly higher in an acid environment, an acid, preferably a mineral and/or an alkylsulfonic acid, is added to the electrolyte in amounts of 140--382 g/L of electrolyte, preferably 175--245 g/L of electrolyte. The use of methanesulfonic acid turned out to be especially advantageous, since for one thing this produces advantageous solubility of metal salts and for another, because of its acid strength, it produces or facilitates the adjustment of the pH needed for the process. In addition, methanesulfonic acid has the advantageous property of contributing considerably to the stability of the bath.

[0020] In accordance with an additional characteristic of the invention at least one additional metal and/or chloride is added to the electrolyte. Advantageously, the metals are in

the form of their soluble salts. In particular, the addition of zinc and/or bismuth has a considerable effect on the properties of the deposited coatings. The metals zinc and/or bismuth added to the electrolyte can namely be in the form of salts of alkylsulfonic acids, preferably as methanesulfonates or as salts of mineral acids, preferably as sulfates. Zinc sulfate is especially preferably used in the electrolytes as zinc salt, and is advantageously added in an amount of 0--25 g/L of electrolyte, preferably 15--20 g/L of electrolyte. Bismuth methane sulfate is especially preferably used in the electrolyte as bismuth salt and is advantageously added to the electrolyte in an amount of 0--5 g/L of electrolyte, preferably 0.05--0.2 g/L of electrolyte.

[0021] In addition, various additives, for example stabilizers and/or complexing agents, oxidation inhibitors and brighteners, that are usually used in acid electrolytes for deposition of tin alloys can be added to the electrolyte.

[0022] In particular, the use of suitable compounds for stabilizing the electrolyte is an important condition for rapid as well as qualitative high grade deposition of bronzes. Gluconates are advantageously added to the electrolyte and stabilizers and/or complexing agents. Here in the method in accordance with the invention the preferred use of sodium gluconate turned out to be especially advantageous. The concentration of the stabilizers and/or complexing agents is 0--50 g/L of electrolyte, preferably 20--30 g/L of electrolyte. Compounds from the class of the dihydroxybenzenes, for example mono- or polyhydroxyphenyl compounds like pyrocatechol or phenolsulfonic acid are preferably used as oxidation inhibitors. The concentration of oxidation inhibitors is 0--5 g/L of electrolyte. Advantageously, the electrolyte contains hydroquinone as oxidation inhibitor.

[0023] The conduct of the method in accordance with the invention enables the deposition of bronzes onto various substrates. For example, all of the usual methods for making electronic components can be used. In the same way especially hard and wear-resistant bronze coatings can be deposited on materials like bearings, etc., to the method in accordance with the invention. The method in accordance with the invention is advantageously also used in the fields of decorative coating of, for example, fixtures and jewelry, etc., where the deposition of multi-component alloys that contain tin, copper, zinc and bismuth is particularly advantageous in these areas.

[0024] A really special advantage is that the so-called "true" bronzes that have a copper content $>60\%$ can be deposited with the method in accordance with the invention, where the copper content can be up to $95\text{ wt}\%$ in each according to the desired properties. In addition, the ratio of the amount of copper to the amount of tin in the electrolyte has a considerable effect of properties like hardness and color of the bronze coatings. For instance, at a tin/copper ratio of 40/60 silver-colored coatings, the so-called white bronzes, which are relatively soft, are deposited. At a tin/copper ratio of 20/80 yellow gold colored coatings result, the so-called yellow bronzes, and at a tin/copper ratio of 10/90 red gold colored coatings are formed, the so-called red bronzes.

[0025] Moreover, the deposition of high-tin white bronzes with a copper content $\approx 10\%$ is also possible.

[0026] In each case according to the desired appearance of the bronze coatings additives such as brighteners are added to the electrolyte, in addition to it having a varying copper content. Advantageously, the electrolyte contains brighteners from the class of the aromatic carbonyl compounds and/or

α,β-unsaturated carbonyl compounds. The concentration of brighteners is 0-5 g/L of electrolyte.

— DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0027] This application claims priority from European patent application number 02022718.7, the entire disclosure of which is explicitly incorporated by reference.

[0028] Some preferred embodiments are presented below for illustration of the invention in more detail, but the invention is not limited to these embodiments.

Electrolyte composition:

— [0029] The base electrolyte of the highly acid electrolyte in accordance with the invention contains essentially (per liter of electrolyte)

2-75 g divalent tin,
2-70 g divalent copper,
2-40 g of an aromatic nonionic wetting agent, and
140-382 g of a mineral and/or alkylsulfonic acid.

— [0030] Optionally, other components can be added to the electrolyte (per liter of electrolyte):

—
0-10 g of an anionic and/or aliphatic nonionic wetting agent,
0-50 g of a stabilizer and/or complexing agent,
0-5 g of an oxidation inhibitor,
0-5 g of a brightener
0-5 trivalent bismuth
0-25 g divalent zinc.

— [0031] In order to achieve a specific color of the deposited bronze coatings the electrolyte is prepared by varying the individual components, as given below as a matter of example. Additional information about the corresponding

process conditions as well as other properties of the individual coatings can be seen in Table 1.

[0032] Example 1 (red bronze)

4 g/L ~~Sn²⁺~~Sn²⁺
18 g/L ~~Cu²⁺~~Cu²⁺
286 g/L methanesulfonic acid
3 g/L aromatic nonionic wetting agent
0.4 g/l aliphatic nonionic wetting agent
2 g/L oxidation inhibitor
20 mg/L complexing agent

[0033] Example 2a (yellow bronze)

4 g/L ~~Sn²⁺~~Sn²⁺
18 g/L ~~Cu²⁺~~Cu²⁺
240 g/L methanesulfonic acid
32.2 g/L aromatic nonionic wetting agent
2 g/L oxidation inhibitor
25 mg/L stabilizer/complexing agent

[0034] Example 2b (yellow bronze)

4 g/L ~~Sn²⁺~~Sn²⁺
18 g/L ~~Cu²⁺~~Cu²⁺
286 g/L methanesulfonic acid
32.2 g/L aromatic nonionic wetting agent
6 mg/L ~~brightener~~mg/Lbrightener
2 g/L oxidation inhibitor
50 mg/L stabilizer/complexing agent

[0035] Example 3 (white bronze)

5 g/L ~~Sn~~²⁺Sn²⁺
10 g/L ~~Cu~~²⁺Cu²⁺
240 g/L methanesulfonic acid
32.2 g/L aromatic nonionic wetting agent
6 mg/L ~~brightener~~mg/Lbrightener
2 g/L oxidation inhibitor
25 mg/L stabilizer/complexing agent

[0036] Example 4 (matte white bronze)

18 g/L ~~Sn~~²⁺Sn²⁺
2 g/L ~~Cu~~²⁺Cu²⁺
258 g/L methanesulfonic acid
9 g/L aromatic nonionic wetting agent

[0037] To improve the hardness and/or ductility of the deposited bronze coatings the contents of zinc and/or bismuth indicated below as examples are added to the electrolyte. Additional data on the corresponding process conditions and other properties of the individual coatings can be seen in Table 1.

[0038] Example 5 (high ductility)

4 g/L ~~Sn~~²⁺Sn²⁺
18 g/L ~~Cu~~²⁺Cu²⁺
238 g/L methanesulfonic acid
32.2 g/L aromatic nonionic wetting agent
3 mg/L ~~brightener~~mg/Lbrightener
2 g/L oxidation inhibitor
25 mg/L stabilizer/complexing agent
20 g/L ~~ZnSO₄~~ZnSO₄

[0039] Example 6 (hardness)

4 g/L ~~Sn2+~~Sn²⁺
18 g/L ~~Cu2+~~Cu²⁺
238 g/L methanesulfonic acid
32.2 g/L aromatic nonionic wetting agent—
2 g/L oxidation inhibitor
25 mg/L stabilizer/complexing agent
0.1 g/L ~~Bi3+~~Bi³⁺

[0040] Example 7 (yellow bronze)

14.5 g/L ~~Sn2+~~Sn²⁺
65.5 g/L ~~Cu2+~~Cu²⁺
382 g/L methanesulfonic acid
32.2 g/L aromatic nonionic wetting agent
4 g/L oxidation inhibitor
25 mg/L stabilizer/complexing agent
20 g/L ~~ZnSO4~~ZnSO₄

_____ [0041] With these exemplary electrolyte compositions coatings with specific properties were deposited under the process conditions listed in the following table.

Exempl e No.	Coating/Amounts in wt%—				Properties of coating			
	Sn	Cu	Zn	Bi	Hardnes s	Ductility	Glos s	Color
1	10	90	-	-	180 HV ₅₀	++	Yes	Red
2a	20	80	-	-	283 HV ₅₀	±	Yes	Yellow
2b	20	80	-	-	317 HV ₅₀	±	Yes	Yellow
3	40	60	-	-	360 HV ₅₀	±	Yes	White

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4	90	10	-	-	-	-	No	White
5	20	80	<1	-	-	+++	Yes	Yellow
6	20	80	-	<1	345 HV ₅₀	-	Yes	Yellow
7	20	80	<1	-	-	++	Yes	Yellow

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Claims

[0042] When introducing elements of the present invention or the preferred embodiment(s) thereof, the articles "a," "an," "the," and "said" are intended to mean that there are one or more of the elements. The terms "comprising," "including," and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

[0043] In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

[0044] As various changes could be made in the above methods and products without departing from the scope of the invention, it is intended that all matter contained in the above description and shown in any accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

WHAT IS CLAIMED IS:

1. A method for electrodeposition of bronzes, with which the substrate to be coated is plated in an acid electrolyte that contains at least tin and copper ions, and alkylsulfonic acid and a wetting agent,

5 which is characterized by the fact that
 an aromatic nonionic wetting agent is added to the electrolyte, which has a concentration of free methanesulfonic acid of at least 290 g/L and layers with a copper content of at least 10%, preferably at least 60%, are deposited from it.

2. A method as in Claim 1, which is characterized by the fact that 2 to 40 g/L of the aromatic, nonionic wetting agent are added to the electrolyte.

3. A method as in Claim 1 or 2, which is characterized by the fact that that ~~2-naphthol~~-naphthol ethoxylate and/or nonylphenol ethoxylate is added to the electrolyte as aromatic nonionic wetting agent.

4. A method as in one of Claims 1-3, which is characterized by the fact that tin or copper ions are added to the electrolyte in the form of a soluble salt, preferably as the salt of an alkylsulfonic acid, preferably as
5 methanesulfonate.

5. A method as in one of Claims 1-4, which is characterized by the fact that 2-75 g/L tin ions are added to the electrolyte.

6. A method as in one of Claims 1-5, which is characterized by the fact that 5-195 g/L tin methanesulfonate are added to the electrolyte.

7. A method as in one of Claims 1--6, which is characterized by the fact that 2--70 g/L copper ions are added to the electrolyte.

8. A method as in one of Claims 1--7, which is characterized by the fact that 8--180 g/L copper methanesulfonate are added to the electrolyte.

9. A method as in one of Claims 1--8, which is characterized by the fact that the deposition takes place at a temperature of 17--25°C.

10. A method as in one of Claims 1--9, which is characterized by the fact that the deposition takes place in a current density range of 0.1--120 A/dm².

11. A method as in one of Claims 1--10, which is characterized by the fact that the deposition takes place in a highly acid medium.

12. A method as in one of Claims 1--11, which is characterized by the fact that the deposition takes place in a pH range <1.

13. An electrolyte for electrodeposition of bronzes containing at least tin and copper ions, and alkylsulfonic acid and a wetting agent,

which is characterized by the fact that

5 the electrolyte contains an aromatic nonionic wetting agent and has a concentration of free methanesulfonic acid of at least 290 g/L and layers with a copper content of at least 10%, preferably at least 60%, are deposited from it.

14. An electrolyte as in Claim 13, which is characterized by the fact that it contains 2--40- g/L of the aromatic nonionic wetting agent.

15. An electrolyte as in one of Claims 13--14, which is characterized by the fact that ~~2-naphthol~~-naphthol ethoxylate and/or nonylphenol ethoxylate is used as aromatic nonionic wetting agent.

16. An electrolyte as in one of Claims 13--15, which is characterized by the fact that it contains tin and copper ions in the form of a soluble salt, preferably as the salt of an alkylsulfonic acid, especially preferably as methanesulfonate.

17. An electrolyte as in one of Claims 13 and 16, which is characterized by the fact that it contains 2--75 g/L tin ions.

18. An electrolyte as in one of Claims 13 and 17, which is characterized by the fact that it contains 5--195 g/L tin methanesulfonate.

19. An electrolyte as in one of Claims 13 and 18, which is characterized by the fact that it contains 2--70 g/L copper ions.

20. An electrolyte as in one of Claims 13 and 19, which is characterized by the fact that it contains 8--280 g/L copper methanesulfonate.

21. An electrolyte as in one of Claims 13--20, which is characterized by the fact that it contains polyethylene glycol and/or anionic surfactants as wetting agents.

22. An electrolyte as in one of Claims 13--21, which is characterized by the fact that it contains bismuth and/or zinc.

23. An electrolyte as in one of Claims 13--22, which is characterized by the fact that it contains a chloride.

24. An electrolyte as in one of Claims 13--23, which is characterized by the fact that it contains a gluconate as complexing agent.

25. An electrolyte as in one of Claims 13--24, which is characterized by the fact that it contains an oxidation inhibitor from the class of the dihydroxybenzenes.

26. An electrolyte as in one of Claims 13--25, which is characterized by the fact that it contains brighteners from the class of the aromatic carbonyl compounds and/or α,β -unsaturated α -unsaturated carbonyl compounds.

27. An electrolyte as in one of Claims 13--26, which is characterized by the fact that it has a pH value <1.

28. An electrolyte as in one of Claims 13--27 containing
2--75 g/L divalent tin
2--70 g/L divalent copper
2--4 g/L an aromatic nonionic wetting agent,
0--50 g/L a stabilizer and/or complexing agent,
0--10 g/L of an anionic and/or nonionic aliphatic wetting
agent,
0--5 g/L an oxidation inhibitor,
0--5 g/L a brightener,
0--5 g/L trivalent bismuth,
0--25 g/L divalent zinc,
at least 140 g/L of an alkylsulfonic acid.

29. A bronze coating prepared by a method for electrodeposition, in particular by a method as in one of Claims 1--10, which is characterized by the fact that it has a copper content $>10\%$, preferably $>60\%$.

METHOD FOR ELECTRODEPOSITION OF BRONZES

ABSTRACT OF THE DISCLOSURE:

[0045] A method for electrodeposition of bronzes, with which the substrate to be coated is plated in an acid electrolyte that contains at least tin and copper ions, an alkylsulfonic acid and a wetting agent, and the preparation of such an electrolyte.